STUDIES OF HIGH–T_c SUPERCONDUCTORS IN Y–Ba–Cu–O CERAMIC SYSTEM

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BULK SUPERCONDUCTORS $YBa_2Cu_3O_{7-x}$ WITH ZERO RESISTANCE AT 90 K AND NARROW T_c TRANSITIONS (3–4 K) WERE SYNTHESIZED. THE EFFECTS OF THE PROCESS PARAMETERS, THE OPTIMUM OF THE SINTER CYCLE AND THE TEMPERATURE DEPENDENCE OF THE RESISTANCE OF $YBa_2Cu_3O_{7-x}$ SAMPLES WERE INVESTIGATED.

Introduction

The discovery of superconducting compounds in the system La–Ba–Cu–O by BEDNORZ and MÜLLER [1] stimulated activity on high–temperature superconductivity, most of the work concentrating on the compound $YBa_2Cu_3O_{7-x}$ since it has a high transition temperature, T_c = 90 K [2]. The discovery of superconducting compounds with even higher transition temperatures (up to 125 K) in the systems Bi–Sr–Ca–Cu–O [3] and Tl–Ba–Ca–Cu–O [4] shows that recent developments in the field of superconducting oxides are very promising.

Most ceramic $YBa_2Cu_3O_{7-x}$ samples are prepared by powder–ceramic techniques, generally involving three main steps: powder preparation and calcining, sintering, and adjustment of the oxygen content [5]. The reactions can be written as

$$Y_2O_3 + 6\ CuO + 4\ BaCO_3 \longrightarrow 2\ YBa_2Cu_3O_{6.5} + 4\ CO_2 \qquad (1173\ K)$$

and

$$4\ YBa_2Cu_3O_{6.5} + 1/4\ O_2 \longrightarrow 4\ YBa_2Cu_3O_7. \qquad (1193–1203\ K)$$

The microstructure is directly affected by the annealing parameters used to obtain the desired oxygen content. Hence, the conditions are of decisive importance as concerns the ultimate mechanical and superconducting properties of the material. The various stages of $YBa_2Cu_3O_{7-x}$ production are dealt with below, and their effects on the superconducting properties are discussed.

Experimental

Powder preparation

The starting compounds were Y_2O_3 (Fluka, 99.9 %), $BaCO_3$ (Reanal, p.a.) and CuO (Merck, p.a.). The morphology of the powders was established with the BET method. The Y_2O_3 and $BaCO_3$ powders consisted of particles with a mean size of 2–4 μm, and the CuO powder of particles 5–10 μm in size (agglomerates). The starting Y_2O_3 , $BaCO_3$ and CuO were mixed in a molar ratio of 1:4:6. The simplest kind of powder preparation, manual dry mixing in a mortar, yielded very inhomogeneous samples. By contrast, very homogeneous powder mixtures (mean particle size approximately 0.7 μm) were obtained by trituration for 2 hours in isopropanol with agate grinding balls (10 mm in diameter). Mixing in an agate mill avoids contamination by the grinding media. The powder mixtures were annealed in air, oxygen and nitrogen atmosphere at 1173 K for 12–24 hours and then cooled to room temperature at 3 K/min. The product was a compact black mass. It was remilled to less than 20 μm grain size. The course of reaction and the formation of $YBa_2Cu_3O_{7-x}$ were studied by X–ray diffraction analysis (Philips–3100) with monochromatized Cu–K_α radiation.

Compacting and sintering

Cylindrical compacts 4 mm thick and 10–12 mm in diameter were prepared for use in the sintering experiments by powder–pressing at 60 MPa. The samples were sintered at 1193 K for 8–10 hours in electric oven (Fig.1), followed by cooling to room in air and oxygen. The sintering properties were investigated by thermal analysis [7,8]. The samples were heat–treated up to 1373 K in a derivatograph (Erdey–Paulik, G–425).

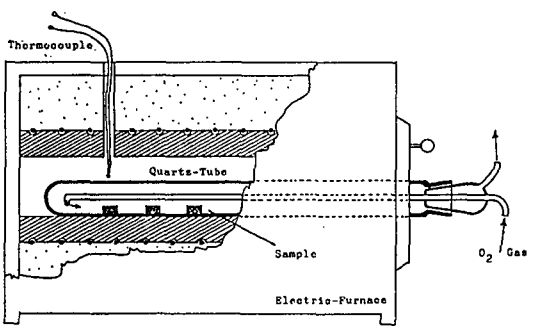

Figure 1: Sintering experiments on specimens in a programmable electrical furnace

The effects of the sintering temperature on the structure and the thermal expansion were studied at 1173 K with an electronic dilatometer (Netzsch), at a heating rate of 5 K/min in air [9]. The microstructure was investigated by means of optical and scanning electron microscopy (JEOL–JSM) with an electron beam–microanalyser to examine several points of the samples.

Superconductivity was first tested *via* the MEISSNER–effect. The transition temperature (T_c) was determined by the resistive four–point method in the temperature range 80–250 K at 0,133 Pa. Thin copper wires were attached to the specimens with conductive silver paint, as power leads and voltage taps. The specimen temperature was measured with a chromel–alumel thermocouple. Resistivity was measured at 10 mA. The four–point voltage was registered with a digital multimeter. For data analysis, a personal computer (ZX–Spectrum) and home–made software were used. This system can measure resistance of samples in vacuum or in any gas atmosphere in the temperature range 77–900 K (Fig.2).

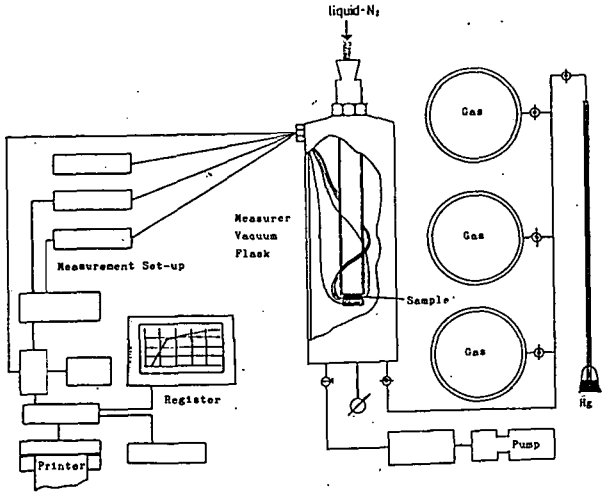

Figure 2. A computer–controlled system for measurement of superconducting samples in vacuum or a gas atmosphere in the temperature range 77–990 K.

Results and discussion

X–ray phase analysis of the powder calcined at 1173 K, indicated the formation of $YBa_2Cu_3O_{7-x}$. After calcination for 2 hours, CuO and Y_2O_3 reflection were no longer observed. The relative intensities of the $BaCO_3$ reflections gradually diminished with increasing time of reaction. The $YBa_2Cu_3O_{7-x}$ phase reflections were observed after 3 hours and the phase formation was almost complete within 4 hours. After compacting, on sintering at 1193 K for 10 hours the reflections of $YBa_2Cu_3O_{7-x}$ very slowly increased in intensity (Fig.3).

The results of derivatographic measurements are shown in Fig.4. Y_2O_3 and CuO did not undergo any change up to 1373 K (Fig.4/1,2). The well–known polymorphic changes of $BaCO_3$ were observed at 1093–1103 K and around 1243 K (Fig.4/3). A significant weight loss and a small endothermic peak were observed in the 1:5 mixture of Y_2O_3 and CuO (Fig.4/4). This weight change may be caused by the reduction of CuO.

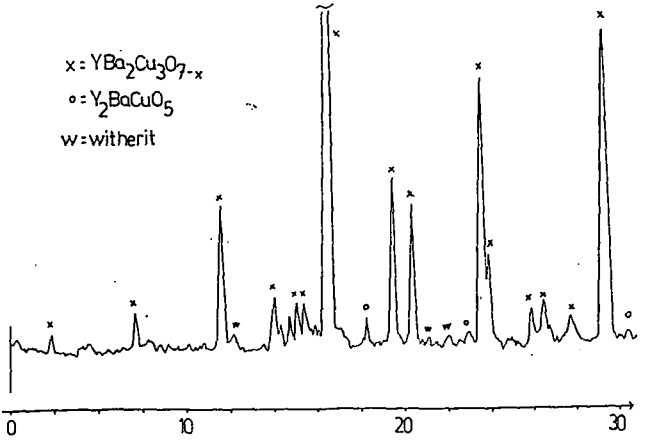

Figure 3: X–ray analysis of superconducting $YBa_2Cu_3O_{7-x}$.

The 1:4 mixture of Y_2O_3 and $BaCO_3$ revealed only the polymorphism of $BaCO_3$ (Fig.

4/5). The 4:6 mixture of CuO and $BaCO_3$ exhibited a chemical reaction at 1263 K (Fig.4/6). The 1:4:6 mixture of Y_2O_3, CuO, and $BaCO_3$ displayed several new endothermic effects (Fig.4/7). The peak at 1133 K is attributed to the perovskite structure transition and the peaks at around 1273 K decomposition.

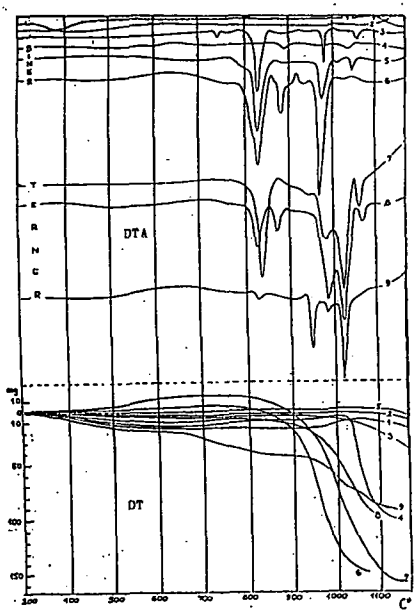

Figure 4: Simultaneous TG and DTA measurements on the starting oxides and their mixtures.

The mixture of the base materials after a 12–24 hours annealing at 1173 K and those compacting and sintering at 1193 K during 4–6 hours exhibit similar decompositions in

the derivatograph oven (Fig.4/8,9).

The different changes in weight during the first two steps in the interval 673–943 K are important. The superconducting properties of the material can change in this temperature range due to oxygen desorption and adsorption and a phase transition from the orthorhombic to the tetragonal state.

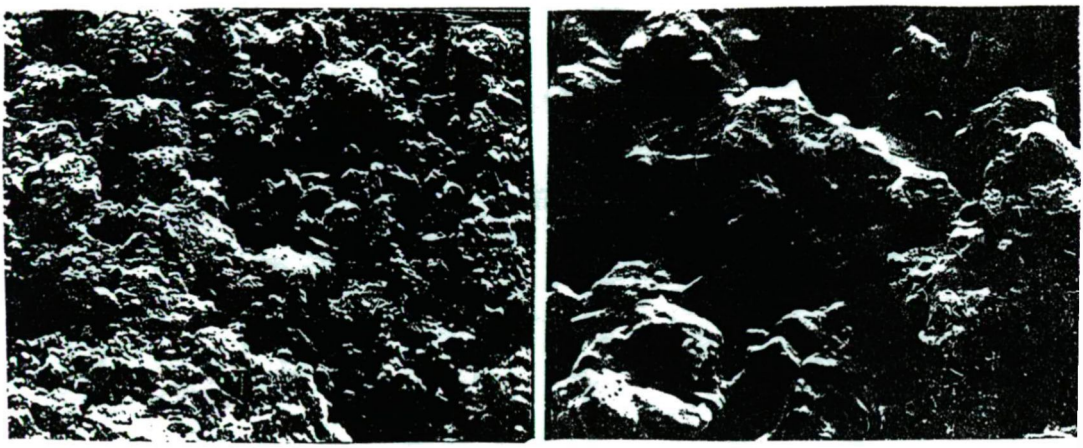

Figure 5: SEM micrographs of a superconducting specimen sintered at 1193 K (M=1050 X and M=13000 X)

The SEM investigations confirmed the results of X–ray diffractometric and thermo–gravimetric analyses. After calcining for 3 hours sinter–necks appear and pronounced grain sets grow (Fig.5).

The sintering conditions exerted marked influence on the microstructure and superconductivity. Specimens sintered at 1173 K displayed a sharp drop in resistance, beginning at about 100 K and reaching zero at 90–85 K. Specimens heat–treated at 1183–1203 K had transition points at 90–92 K (Fig.6/6,7). Samples sintered at 1213 K or higher did not become superconducting. The change in superconductivity at elevated

temperatures can be seen in connection with the formation of liquid phase that separates the superconductive particles.

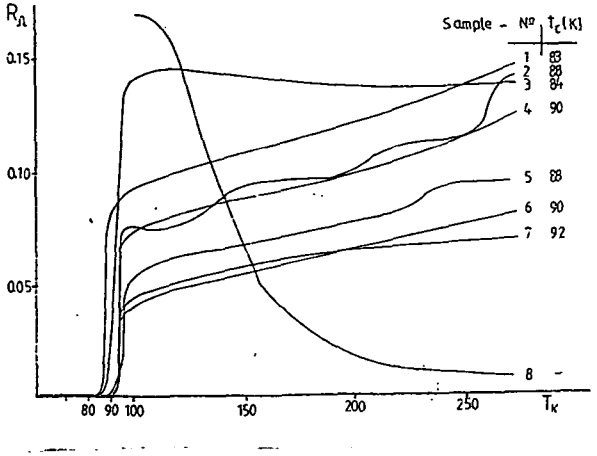

Figure 6: Resistivity as a function of $YBa_2Cu_3O_{7-x}$ specimens sintered at 1173–1213 K.

Dilatometric measurements on the sintered material indicated the existence of a liquid phase. Beginning at 1093 K such specimens showed a rapid increase in shrinkage that could not be attributed to solid–phase sintering. There was an enormous difference in dilation behaviour within a small temperature range (Fig.7). Since the composition of $YBa_2Cu_3O_{7-x}$ is situated very close to the melting zone, even a slight local stoichiometric deviation in Y_2O_3 deficit suffices to cause the formation of a liquid phase.

Heat treatment makes the high–temperature grain boundary phase crystallize extensively into $YBa_2Cu_3O_{7-x}$ thereby restoring the integrity between the superconducting particles and hence converting the specimens into superconductors.

Porosity examination (by water absorption) of the specimens revealed a porosity of 18–25 % caused in part by the formation of carbon dioxide during sintering. The porosity could be reduced by optimizing the calcining conditions.

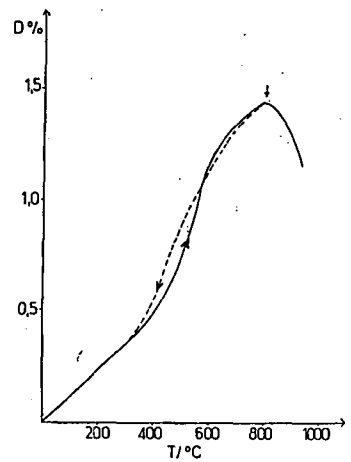

Figure 7: Thermal expansion of superconducting $YBa_2Cu_3O_{7-x}$

SEM and dilatometric measurement demonstrated the phase states which are important for the preparation of superconducting ceramics. The thermal expansivity was also sensitive to temperature change (Fig.7).

Single–phase specimens were obtained only within a narrow temperature range

(1173–1203 K). The broad resistance transitions of specimens sintered below 1183 K indicated the presence of nonsuperconducting volume fractions in such samples (Fig.6/2).

Summary

Reproducible single–phase superconducting ceramic material was obtained by optimizing the various preparation steps. Each individual preparation step exerted a substantial influence on the structural formation and hence on the conducting properties. A homogeneous powder mixture is an important prerequisite for rapid and complete reaction. Investigation of the reaction during calcining revealed the relative rapid formation of a superconducting phase. A single–phase was obtained only within a narrow temperature range. The liquid phase appearing at approximately 1203 K contributed substantially to specimen densification. Slow cooling of the samples after sintering led to the uptake of oxygen and the formation of a superconducting structure.

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